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(Translation)

Japanese Laid-Open Publication No. 1-249333

Laid-Open Publication Date: October 4, 1989

Title of the Invention: Glass cloth for laminate and laminate

Application Number: 63-75856

Filing Date: March 31, 1988

Inventors: F. Nagamine and Y. Sato

Applicant: Nitto Boseki Co., Ltd.

Specification

1. Title of the Invention

Glass cloth for laminate and laminate

2. Claims

(1) A glass cloth for a laminate, wherein at least one of warp and weft constituting the glass cloth is formed of an untwisted glass yarn having a weight of 2.5 to 240 g/1,000 m. = tex

(2) A laminate formed by impregnating a glass cloth with a resin and then curing the resin, wherein the glass cloth according to claim 1 is used as at least one glass cloth layer.

3. Detailed Description of the Invention

[Field of the Invention]

The present invention relates to a laminate preferably used as a base plate of a printed circuit board or the like

and a glass cloth used for the laminate.

[Prior Art]

Conventionally, laminates formed by impregnating a glass cloth with a thermosetting resin such as an epoxy resin and thermally pressing a lamination of several to several tens of such glass cloth layers have been widely used as printed circuit boards for electronic equipment.

The glass cloth used for such a laminate is produced in the following manner. First, a glass material melted in a furnace is introduced to a section having 50 to 2,000 nozzles on a bottom surface. The melted glass material is electrically heated by the section, which is referred to as a bushing. The melted glass is pulled out at a high speed from the nozzles provided on the bottom surface, thereby forming glass fibers. Such fibers receive a light spray of water and pass through an applicator. Then, a sizing agent is applied to the fibers for the purpose of protection, lubrication and binding of the fibers. Next, the fibers are formed into fiber strands by a gathering shoe. The number of fibers included in each fiber strand is adjusted as necessary. One strand may be further divided into a plurality of strands including a few fibers. Strands are continuously wound around a paper or plastic tube mounted on a cylinder rotating at a high speed. The strands are thus rolled in while being moved back and forth in a direction perpendicular to the direction in which the strands are wound at a small angle so as to allow the strands to be easily unwound in a later step, thereby forming a cake. The strands are pulled out from the cake formed in this manner and twisted so as to form twisted

yarns. The resultant twisted yarns are used for forming the glass cloth.

As an apparatus for twisting the strand, a ring twister is usually used. A strand is pulled out from the cake provided to a creel in a direction crossing the direction of the strand so as to avoid damaging the fibers, and then supplied to a traveller by rotation of a feed roller or the creel itself. While being twisted, the strand is rolled in a bobbin secured around a spindle which is rotating at a high speed. Since the strand is rolled around the spindle rotating at a high speed, the amount of strand which can be rolled in one bobbin is limited. Usually, 4 to 8 kg of strand is rolled.

About 400 to 4,000 yarns which are twisted in this manner are warped as warp yarns in the warping step, and then rolled around a warp beam. At this point, a secondary size (mainly including poval or starch powder) is attached to the warp yarns in order to protect the warp yarns from abrasion while the yarns are woven. Then, in the weaving step, the warp beam is set to a loom, and a glass cloth is woven using yarns which are twisted in the same manner as weft yarns. The glass cloth used for printed circuit boards today are mostly plain woven. As the loom, an air-jet loom is used. The glass cloth which has just been woven still has the sizing agent and the like adhering thereto. In the case where such an agent causes a problem in the adhesion with the resin, the organic materials adhering to the glass cloth are removed by heating. (This process is referred to as degreasing.)

The glass cloth obtained as a result of removing the adhering materials from the surface thereof by degreasing is surface-treated by a coupling agent suitable for a resin used as the matrix. Then, the glass cloth is impregnated with an epoxy resin or the like. Several to several tens of such glass cloth layers are laminated and thermally pressed. Thus, a laminate is produced.

[Problems to be Solved by the Invention]

However, in the glass cloth produced in the above-described manner, the warp yarns and the weft yarns are twisted. Therefore, the cross sections of both the warp yarns and weft yarns are helical, and not very flat. Accordingly, it takes an excessively long time to impregnate the glass cloth with a resin, thus causing the problems such as low productivity and also low quality of the resultant laminate caused by air bubbles remaining in the laminate. Furthermore, since neither the warp yarns nor the weft yarns are flat, there is a gap between two adjacent warp yarns and between two adjacent weft yarns. Therefore, the resulting glass cloth has some areas devoid of glass fibers. The laminate formed of such a glass cloth has an inferior surface roughness, which causes a small-diameter drill used for processing the laminate to bend. When a standard-diameter drill is used, the wall of the holes becomes excessively rough.

When the laminate formed of the conventional glass cloth is thin, another problem is presented that the laminate is warped or twisted by the twist of the yarns.

Recently, printed circuit boards for which the lamina-

tes are mainly used are demanded to have higher and higher performance as the high density automatic mounting technology is increasingly advanced. Under such circumstances, the above-described problems have become more serious.

Conventionally, various proposals are made to solve the problems. For example, as a method for causing the glass fiber to distribute to the entire glass cloth to a maximum possible degree and also impregnating the glass cloth with a resin more efficiently, it is proposed that, after the glass cloth is woven, the twisted yarns forming the glass cloth are processed by mechanical means, thereby loosening the fiber strands to make a gap among the fibers. (See, for example, Japanese Laid-Open Publication Nos. 62-156945 and 61-194252.)

Such a method has a disadvantage in terms of production of requiring an extra processing step. Moreover, the conventional twisted yarns used for weaving the glass cloth are generally twisted 0.7 to 5 times/25 mm, and therefore, after the glass cloth is woven, the warp yarns and the weft yarns bind each other. For these reasons, the fiber strands are difficult to loosen. Accordingly, the above-mentioned mechanical processing requires an excessively long time and still the fiber strands are not loosened sufficiently. The fiber strands are especially difficult to loosen at the locations where the warp yarns and weft yarns contact each other. Thus, the glass cloth cannot be impregnated at improved efficiency.

It is known that the twist of the yarns used for weaving the glass cloth causes the warp and twist of the

laminate. In order to prevent such an influence of the twist of the yarns, it is proposed that the glass cloth used for the laminate is woven by combining right-twisted yarns and left-twisted yarns so as to cancel the twisting moments of the two types of yarns, thereby preventing generation of warp. (See, for example, Japanese Laid-Open Utility Model Publication Nos. 54-55958 and 61-22160.)

However, in order to use the right-twisted yarns and left-twisted yarns in combination, it is necessary to arrange warp yarns twisted in different directions in a prescribed order so as to cancel the twisting moments in the step of winding a great many warp yarns around the beam. This requires much care and labor. In addition, weaving the glass cloth by arranging the right-twisted and left-twisted yarns so as to cancel the twisting moments of the two types of warp yarns and also the twisting moments of the two types of weft yarns is not very effective because of the following way of weaving the glass cloth of an air-jet loom, which is used today for weaving glass cloth for laminates. A weft yarn is caused to jump from one end of the warp yarn array to the other end by air-jet; and when the weft yarn reaches the other end, the end of the yarn is wedged and the yarn is cut, and then another weft yarn is caused to jump in the same direction and the same process is repeated. The weft yarn is not turned back in the opposite direction as is when a shuttle loom is used. Since both ends of the yarns are free, the yarns are easily untwisted. The twist of the weft yarns which have been wedged is held by the warp yarns, but the holding force becomes weaker toward the ends. For example, a weft yarn which is twisted 1 times/25 mm in a middle part is

twisted only 0.6 times/25 mm at the ends. Such a defect cannot be avoided by any conventional method.

The present invention has an objective of providing a glass cloth free from the defects of the conventional glass cloth, i.e., inefficient impregnation of the glass cloth with a resin, non-uniform distribution of the glass fibers in the glass cloth, and twist in the glass cloth causing the warp and twist of a thin laminate formed of the glass cloth, and also providing a laminate formed of such a glass cloth.

[Means for Solving the Problems]

As a result of various studies, the present inventors found that (1) in order to obtain a glass cloth which can be impregnated with a resin with satisfactory efficiency and has less twist, it is much more effective to use an untwisted yarn than to loosen the twisted yarn after being woven into a glass cloth; and (2) a glass cloth can be produced even using a untwisted yarn.

Conventionally, as described above, the glass cloth for laminates is formed of twisted yarns. A shuttle loom was used for weaving the glass cloth in the early days. When a shuttle loom is used, the glass fibers wound in the shuttle are easily damaged, and untwisted yarns are easily separated and have fluff and thus cannot be woven into a good quality glass cloth. Thus, inevitably, twisted yarns are used. Because of such historical background, it is considered that untwisted yarns cannot be woven in a satisfactory manner even today, i.e., after various other looms such as an air-jet loom and a water-jet loom have

been developed. Accordingly, twisted yarns are commonly used. Conventionally, roving formed by binding a plurality of strands is used.

A roving cloth for FRP is formed of untwisted glass fiber rovings for both warp and weft. Such a roving cloth, which is usually woven by a rapier loom, includes a small number of warp yarns and weft yarns and has a largely uneven surface. Such a roving cloth cannot be used for printed circuit boards, which are preferably formed of a thin cloth including a large number of warp yarns and weft yarns (i.e., having high density); nor is roving cloth conventionally intended to be used for printed circuit boards. Accordingly, conventionally there is no idea of weaving the glass cloth for printed circuit boards using untwisted yarns.

The present inventors, as a result of experiments, found that it is possible to weave the cloth using untwisted glass yarns by an air-jet loom, probably due to the recent improvement in the glass fiber quality, sizing agent quality, performance of the loom, and the like. After various studies, the present inventors completed the present invention.

The present invention has been made based on the above-described findings. A first invention in the present application relates to a glass cloth for a laminate, wherein at least one of warp and weft constituting the glass cloth is formed of an untwisted glass yarn having a weight of 2.5 to 240 g/1,000 m.

A second invention in the present application relates to a laminate formed by impregnating a glass cloth with a resin and then curing the resin, wherein at least one of warp and weft constituting at least one glass cloth layer is formed of an untwisted glass yarn having a weight of 2.5 to 240 g/1,000 m.

The untwisted glass yarn used according to the present invention is formed by binding a great many glass filaments without twisting. Specifically, the glass fiber strand usable according to the present invention is produced by pulling out melted glass filaments from a plurality of nozzles in the bushing at a high speed, applying a sizing agent to the melted glass filaments, binding the filaments and then winding the filaments around a paper or plastic tube by a winder. (Such glass fiber strand corresponds to the strand before being twisted in the conventional method for producing the twisted yarn for the glass cloth.) A cake is formed by winding the strands around the paper or plastic tube. After the sizing agent adhering to the glass fibers is dried, yarns are pulled out from the cake and warped in the conventional manner and wound around a beam to be used as warp yarns. Such yarns can be also used as weft yarns. When such strands are used for weft, it is not necessary to specifically dry the sizing agent. The yarns can be dried by continuously passing the yarns through a drier provided before the yarns guide of the loom.

According to the present invention, the untwisted glass yarns may be used for either the warp or weft, or both of the warp and weft. In the case where untwisted glass yarns are used only for the weft and twisted yarns

are used for the warp, the twisted yarns having the same twisting direction can be used for the warp in order to obtain a glass cloth achieving the objective of the invention. In the case where the right-twisted yarns and left-twisted yarns are combined to be used for the warp, the twisting moments of the two types of yarns are cancelled and thus a still better glass cloth can be obtained. In the case where the untwisted yarns are used for both the warp and weft, the glass fibers are bound only loosely and easily separated. Accordingly, the glass cloth produced in this manner can be impregnated with a resin efficiently. Moreover, since the untwisted yarns do not have a twisting moment, the laminate formed of such a glass cloth is not warped or twisted by the twist of the yarns.

As the sizing agent used for the untwisted glass yarns, various known agents can be used in accordance with the purpose of the glass cloth, the type of the drier, the drying temperature and the like. A recently developed non-desizing sizing agent, which does not require degreasing or surface treatment, eliminates the necessity of twisting, degreasing, and surface treatment. Accordingly, the economic aspects of the production, e.g., productivity and production yield are significantly improved.

As the loom used for weaving the glass cloth using the untwisted glass yarns, any known loom can be used as long as the untwisted yarns are not damaged and the glass cloth can be woven as closely as desired. For example, an air-jet loom, a water-jet loom, a shuttle loom, and a rapier loom can be used. Among these types of looms, the air-jet loom is preferable in terms of the quality of the glass

cloth and productivity. In the case where the air-jet loom is used, the untwisted yarns used as the weft yarns are exposed to less friction and thus less damaged. The air-jet loom has further advantages of a higher weaving speed and higher productivity.

Regarding the count of the untwisted yarns used according to the present invention, excessively thin yarns undesirably lower the productivity. Excessively thick yarns result in a roughly woven glass cloth and reduce the quality of the laminate, and also are separated when being woven to make the weaving procedure difficult. In consideration of these points, the untwisted yarns of 2.5 to 240 g/1,000 m are usually selected, and preferably the yarns of 5.6 to 135 g/1,000 m are used.

Function

A glass cloth according to the present invention uses untwisted glass yarns for at least one of the warp and weft. The untwisted yarns, which are not bound by the twist, are easily deformed by the external force generated when the yarns are woven into the glass cloth. In the woven glass cloth, the untwisted yarns are flat at the intersections of the warp yarns and the weft yarns, and exist in the cloth in a separated state. Accordingly, the glass cloth can be impregnated with a resin at satisfactory efficiency. The contact faces of the warp yarns and the weft yarns are most difficult to be impregnated with a resin since the resin needs to go through the warp yarns or the weft yarns. According to the present invention, since untwisted yarns are used for at least one of the warp yarns and the weft yarns, the contact faces can be impregnated

with a resin rapidly through the untwisted glass yarns which are easily impregnated. Therefore, compared to the conventional glass cloth in which both the warp and weft are formed of twisted yarns, the glass cloth according to the present invention is impregnated with a resin at a significantly higher speed.

Further according to the present invention, due to the flat untwisted glass yarns, the size of the gap between two adjacent warp yarns and between two adjacent weft yarns is decreased, and thus the glass fibers are distributed throughout the entire glass cloth. Therefore, the areas devoid of glass fibers are significantly reduced. This makes movement of the glass fibers in the cloth difficult, thereby tending to avoid generation of non-uniform weaving while the cloth is handled. Such a cloth is easy to handle. Moreover, a laminate formed of such a closely woven glass cloth has a small surface roughness and is easily processed by a drill.

The glass cloth according to the present invention can also be treated by mechanical processing for separating the warp yarns and weft yarns as is conventionally performed. The same effect can be obtained in a shorter period of time with less processing than the conventional glass cloth. Accordingly, the glass cloth is less damaged and so can retain an inherent strength of the glass.

The glass cloth according to the present invention using untwisted yarns for at least one of the warp and weft is less influenced by the twist of the warp or weft. A laminate formed of such a glass cloth is less warped and

less twisted.

Use of the untwisted yarns for the glass cloth according to the present invention has the following advantages in the production and quality of the glass cloth.

In the case where a twisted yarn is conventionally formed of glass strands, the glass strands are formed into a cake by a glass spinning apparatus and yarns are pulled out from the cake. In order to twist the yarns, the yarns are passed through a traveller which rotates around a bobbin at a high speed and then wound in the bobbin. While the yarns are passed through the traveller, the filaments are cut and this causes fluff. Since it is not necessary to perform such a process in the case of untwisted yarns, the filaments are not cut and thus the resultant cloth has less fluff. In the twisting step, a yarn having a weight of 67.5 g/1,000 m is produced in the amount of 0.5 to 1 kg/hour, and 3 to 8 kgs of yarn is usually wound in one bobbin. Such a twisting step requires a great number of twisting apparatuses and workers. The untwisted yarn used according to the present invention does not need such a step and has significantly higher productivity.

The untwisted glass yarn used in the present invention is substantially the strand before the twisting step, and as much as 20 kgs or more of the yarn can be rolled in from one cake. Due to such a large amount of yarn which can be rolled in at one time, the following advantages can be obtained in the production of the glass cloth.

The glass cloth used for a printed circuit board should not have stitches, since the stitch parts of the cloth, which are thicker than the other parts of the cloth, damage the copper foil when the printed circuit board is formed by pressing and thus causes disconnection of the circuit. Accordingly, automatic switching of the weft yarns which is used for producing synthetic fiber cloth cannot be used. When the loom is out of yarn, the loom is automatically stopped. In order to supply additional weft yarn, the troublesome procedure of manually exchanging the bobbins and setting the loom from the start is performed today. The glass weft yarn in general use is wound around one bobbin in the amount of 4 to 8 kgs. From the cake according to the present invention, about twice to five times the amount of yarn can be wound. Thus, the number of times the yarns need be connected is drastically reduced to shorten the period during which the loom is stopped.

(Examples)

Hereinafter, the present invention will be described with reference to examples.

Example I

Melted glass was pulled out from a 200-hole bushing, thereby forming glass fibers having a diameter of 7 μ m. The fibers were passed through an applicator, and then a starch-type sizing agent for yarns was applied for the purpose of protection and binding of the glass fibers. The fibers were formed into one strand by a gathering shoe, and then 12 kgs of the strand was wound around a paper tube having a diameter of 200 mm while being moved back and forth in a direction perpendicular to the direction in

which the strand is wound, thereby forming a strand cake. The cake was put into a drier and dried at 105°C for 20 hours. The strand, i.e., the untwisted yarn produced in this manner was used for the weft for weaving a glass cloth. The warp yarn was produced as follows. Two hundred filaments each having a diameter of 7 μ m were bound, and the same sizing agent was applied to the resultant yarn. Then, while the yarn was left-twisted 1 times/25 mm while being unwound and rolled in a bobbin as a usual twisted yarn. Then, the yarn was treated by warping and wound around a beam to be used as a warp yarn. The number of yarns used and other conditions for weaving are as shown in Table 1.

Before weaving, the untwisted glass yarn cake for the weft was set in a weft yarn supply apparatus provided in the vicinity of the air-jet loom.

After the untwisted glass yarn pulled out from the cake was passed through the yarn guide, the length of the untwisted glass yarn was measured, temporarily stored in a pool pipe, and then fixed in the warp yarn opening by air-jet from the nozzles. Thus, the cloth was produced. The cloth was processed by the same degreasing and surface treatment as performed for a glass cloth which is used as a general resin composite material. Then, the cloth was tested for physical properties. The results are shown in Table 2.

Example II

Melted glass was pulled out from a 800-hole bushing, thereby forming glass fibers having a diameter of 9 μ m. As

in Example 1, 16 kgs of the strand was wound around a paper tube having a diameter of 300 mm while being moved back and forth in a direction perpendicular to the direction in which the strand is wound.

The cake was set in a weft yarn supply apparatus provided in the vicinity of the air-jet loom without being dried. An untwisted glass yarn was pulled out from the cake and continuously dried through the high-frequency hot-air drier provided before the yarn guide. Then, the glass yarn was passed through the yarn guide and supplied to the loom.

For the warp, left-twisted and right-twisted yarns shown in Table 1 and warped so as to be arranged alternately were used. The resultant glass cloth was degreased and surface-treated by epoxy silane, and then tested for physical properties. The results are shown in Table 2.

Example III

Using the same procedure as in Example II except that the 400-hole bushing was used, sixteen kilograms of the strand with no twist was wound around a paper tube having a diameter of 186 mm while being moved back and forth in a direction perpendicular to the direction in which the strand is wound. The cake was dried at 50°C for 12 hours by a vacuum, low temperature, high-frequency drier. The yarn pulled out from the cake was used for the warp and weft to form a glass cloth. The glass cloth was treated in the same way as in Example II, and then tested for physical properties. The results are shown in Table 2.

Comparative example I

A left-twisted yarn of 22.5 g/1,000 m twisted 1 times/25 mm used for the warp in Example I was used for the warp and weft to produce a glass cloth. The glass cloth was treated in the same way as in Example I and then tested for physical properties. The results are shown in Table 2.

Comparative example II

The strand rolled in as described in Example III was left-twisted by a usual method to form a yarn of 67.5 g/1,000 m twisted 1 times/25 mm. The yarn was used for the warp and weft to form a glass cloth. The glass cloth was treated in the same way as in Example III and then tested for physical properties. The results are shown in Table 2.

Example IV

A printed circuit board was produced using the glass cloth described in each of Examples II and III.

The epoxy resin used for producing a sample printed circuit board was as follows.

Epicoat 1001	100 weight parts
(epoxy resin produced by Shell Chemical)	
Dicyandiamide	2 weight parts
Benzyldimethylamine	0.2 weight parts
Solvent	100 weight parts

The glass cloth was impregnated with a varnish of such an epoxy resin and dried to obtain a prepreg. Eight of such prepreps were laminated and pressed at a pressure of

50 kg/cm² at 170°C for 90 minutes, thereby obtaining a laminate having a thickness of 1.7 mm and a planar size of 450 x 450 mm.

The warp and twist of the laminate were measured by a test method described in JIS, C, 6481, 5.4.3. The results are shown in Table 3.

Comparative example III

A laminate was produced using the glass cloth described in Comparative example II under the same conditions as in Example IV. The warp and twist of the laminate were measured by the same method. The results are shown in Table 3.

As can be appreciated from Table 2, the glass cloth according to the present invention is superior in impregnation efficiency. As can be appreciated from Table 3, the laminate formed of a glass cloth according to the present invention is less warped and less twisted.

Table 1

	Diameter of single yarn (μm)	Count (g/1000m)	Number of yarns		Warp yarn		Weft yarn	
			Warp yarn (per 25 mm)	Weft yarn (per 25 mm)	Number of twists (times/25 mm)	Twisting direction	Number of twists (times/25 mm)	Twisting direction
Example I	7	22.5	59	57	1	left	none	none
II	9	135.0	20	20	1	right, left	none	none
III	9	67.5	44	37	none	none	none	none
Comparative example I	7	22.5	59	57	1	left	1	left
II	9	67.5	44	37	1	left	1	left

Loom: air-jet loom

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Yarn guide width: 1250 mm

Rotation rate of the loom: 400 rpm

Table 2

	Ventilation (cc/cm ³ /sec)	Impregnation efficiency (period of time)
Example I	19.0	8 min. 11 sec.
II	4.2	10 min. 07 sec.
III	2.5	7 min. 25 sec.
Comparative example I	52.0	17 min. 38 sec.
II	10.7	15 min. 42 sec.

Ventilation: conformed to JIS, L, 1096 (Ventilation test: method A)

Impregnation efficiency: 50 cc of epoxy resin varnish was dropped on a cloth of 10 × 10 cm, and the time until the cloth was completely impregnated with the resin was measured.

Table 3

	Glass cloth used	Warp		Twist	
		Before heating	After heating	Before heating	After heating
Example IV	Example II	1.0	1.5	6.0	7.5
	III	1.0	1.2	4.0	5.3
Comparative example III	Comparative example II	2.0	3.5	10.5	14.5

Warp and twist: Measured by the method described in JIS, C, 6481, 5.4.3.

Sample size: 450 x 450 mm

Heating condition: 170°C for 30 minutes

[Effect of the Invention]

As described above, the glass cloth for a laminate according to the present invention uses an untwisted yarn of 2.5 to 240 g/1,000 m for at least one of warp and weft. Therefore, the glass cloth includes untwisted yarns distributed in a flat state in the entity thereof, and thus can be impregnated with a resin efficiently. Using such a glass cloth, a high quality laminate including no air bubbles therein can be obtained at high productivity. The production process of the glass cloth can be simplified by using the untwisted yarn, compared to the conventional cloth formed of twisted yarn, thereby improving the productivity.

The glass cloth according to the present invention has smaller areas devoid of glass fibers, i.e., is closely woven. A laminate according to the present invention formed of such a glass cloth has a satisfactory surface roughness and is easily processed by a drill. Since the glass cloth includes a smaller amount the twisted yarn, the laminate is less warped and less twisted. Accordingly, the laminate according to the present invention has satisfactory characteristics to be used for a printed circuit board, and can be processed by a high density automatic mounting apparatus.